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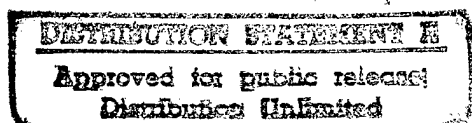
Dear Dr. Ferek:

On behalf of Dr. John W.H. Dacey and Dr. Nelson M. Frew, please find enclosed three copies of the Final Technical Report for ONR Grant N00014-95-1-0817, entitled "Laboratory Measurements of the Water/Air Flux of Dimethylsulfide Using a Wind/Wave Tank".

If there is anything else which you require, please let me know.

Sincerely,

Jane E. Marsh  
Sr. Staff Assistant  
Biology Department



enclosures

xc: S. Ferreira, WHOI Grant & Contract Services  
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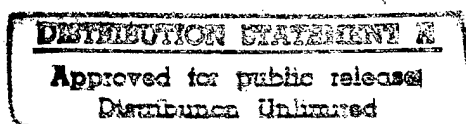
Laboratory Measurements of the Water-Air Flux of Dimethylsulfide using a Wind Wave Tank  
J. W. H. Dacey and N. M. Frew

Estimating the flux of dimethylsulfide (DMS) from the ocean to the atmosphere is an important biogeochemical problem (Andreae and Crutzen 1997). Sulfur aerosols are an important contributor to optical haze in the marine atmosphere as well as a possible modulator of global climate. Shaw (1983, 1987) first suggested that atmospheric sulfur might be involved in climate regulation. Charlson *et al.* (1987) proposed that volatile organic sulfur emitted from the ocean was involved in the formation of cloud condensation nuclei, affecting the albedo and radiation balance of the earth. Charlson *et al.* (1992) estimated that the direct (backscattering and reflection of solar radiation by sulfate aerosols) and indirect (cloud albedo) effects of sulfate aerosols might counteract the climatic forcing by trace greenhouse gases. The relative roles of greenhouse gases and sulfate aerosols in global atmospheric change remain a topic of debate (Schwartz, 1988; Caldeira, 1989; Falkowski *et al.* 1992; Langner *et al.*, 1992; Kiehl and Briegleb, 1993; Bates *et al.*, 1997).

Dimethylsulfide (DMS) is the most abundant volatile sulfur compound in seawater and is widely accepted as dominating the flux of biogenic sulfur to the atmosphere: it constitutes about half of the global biogenic sulfur flux to the atmosphere (Andreae, 1990; Erickson *et al.*, 1990). The concentrations of DMS in the surface mixed layer of the ocean are orders of magnitude higher than the equilibrium concentration in the marine atmospheric boundary layer. Thus, a strong concentration gradient exists to drive a flux of DMS into the atmosphere (Andreae, 1986; Bates *et al.*, 1987). The sea-air exchange of DMS is affected by a number of physical factors, including seawater temperature, wind speed, surface turbulence and gas diffusivity (Liss and Merlivat, 1986; Wanninkhof, 1992; Saltzman *et al.*, 1993). Saltzman and Cooper (1989) concluded, based on variations in DMS concentrations in the atmospheric marine boundary layer, that DMS transfer may be slower than predicted by the standard Liss-Merlivat transfer model. A more recent assessment by Yvon *et al.* (1996) suggests that flux may be higher than these flux models predict. All estimates of DMS flux have depended on the assumption that DMS flux is water-side controlled, although the relatively high solubility of DMS suggests that its behavior may be transitional to air-side control.

The flux of gases across the air-water interface is understood to involve three transfer processes (Liss and Slater, 1974): (1) transfer from the bulk aqueous solution to the surface water film, (2) transfer from the surface water film to the surface air film, and (3) transfer from the surface air film to the bulk atmosphere. The rate of gas equilibration at the interface between air and water films is taken to be faster than transport through the sublayers on either side of the interface. The rate of transport is therefore controlled by transport to or from the interface through the viscous sublayers in the water and in the air. The relative importance of the hydrodynamics of these sublayers is determined by a number of factors.

The rate of transfer of relatively insoluble permanent gases between the water and the atmosphere is controlled by the flux through the water-side boundary layer. Mass balance equations indicate that higher gas solubility increases the significance of the air-side control of flux, as the rate of equilibration between the water and the surface air film has a disproportionate

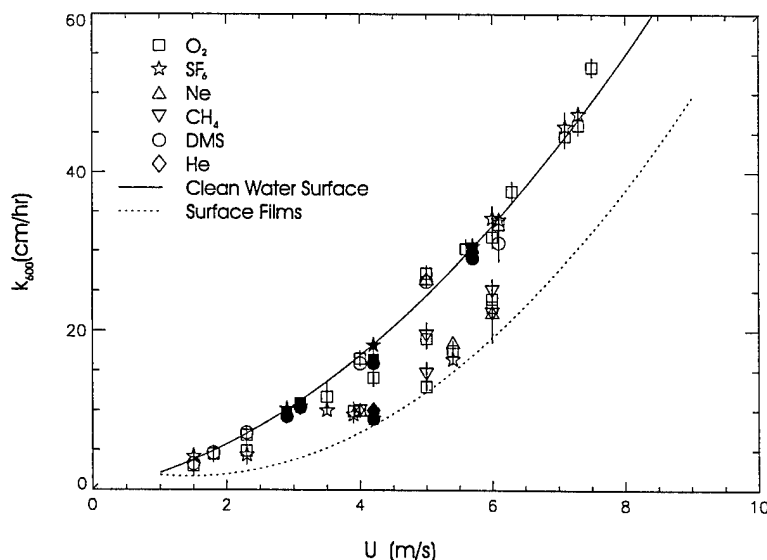


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impact on the fugacity on the air-side boundary. The transfer of a relatively few molecules quickly diminishes the partial pressure gradient across the interface. The fluxes of highly soluble gases, such as methylamines, ammonia and water vapor itself are controlled by flux through the air-side sublayer.

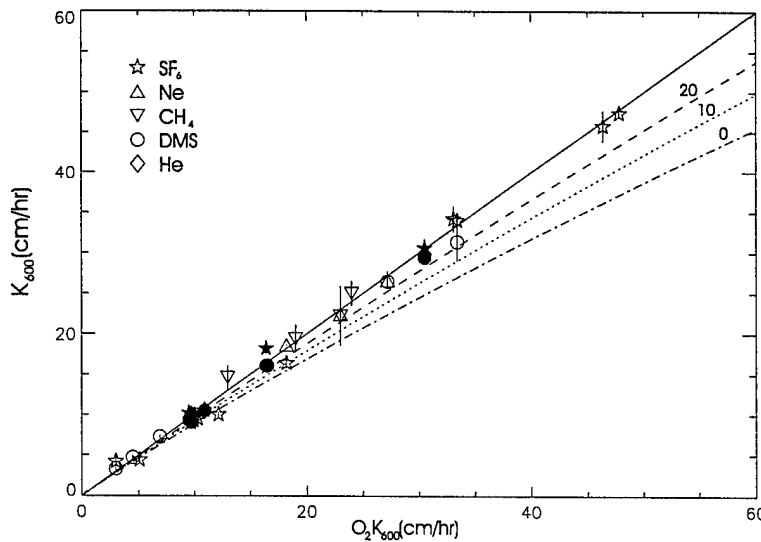
Our main objective in this project were to parameterize the flux kinetics of DMS while simultaneously measuring water-air transfer of  $O_2$ ,  $SF_6$ , Ne,  $CH_4$ , and He under varying wind speeds and hydrodynamic conditions. The experiments were designed to allow investigation of the air-side transfer resistance and the role of surface films in regulating DMS flux.

Experimental estimates of  $k_{600}$  for gases measured in this study are plotted in Figure 1. The data follow the non-linear pattern of increasing flux with increased wind speed familiarized by Liss & Merlivat (1986). Data in Figure 1 cannot be compared directly with the Liss-Merlivat plot since the wind speed in our tank experiment is measured at 10 cm, as opposed to 10 m elevation. Our data are revealing, however, in illustrating the source of some of the variability in laboratory and field measurements. The variability in flux we observed under similar wind speeds indicates that wind speed is not the sole factor determining flux through the sublayers. In the case of water-side controlled gas flux, the hydrodynamics of the aqueous sublayer is key, and these hydrodynamics are significantly controlled by wind stress,  $u_*$ . In the field, the relationship between  $u_*$  and  $u$  introduces some variability, since  $u_*$  depends not only on wind speed, but also on other factors such as sea state. This does not explain the variability in the wave tank, however, where the fetch is essentially infinite and the wave field is established quickly and remains constant during an experiment.



**Figure 1** Laboratory wind-wave tank measurements of gas transfer velocity ( $Sc=600$ ) versus wind speed ( $z=10$  cm) for  $O_2$ ,  $SF_6$ , Ne,  $CH_4$ , DMS, and He. Data represented as open symbols and solid symbols were measured in fresh water and seawater, respectively. Fitted lines to the laboratory measurements of Frew *et al.* (1995) are shown for comparison. The upper bound on the data lies near the clean water data of Frew *et al.* The lower bound on the data lies near experimental data with surface films (0.03  $\mu M$  Triton-X 100). Standard errors are plotted for each point.

Other factors control the relationship between  $u_*$  and  $k_{600}$ , most notably variability in the physical characteristics of the water surface due to surfactants. Small changes in the concentration of surfactant strongly influence the hydrodynamics of the aqueous sublayer (Frew et al., 1995). This variability can be factored out through the dual-tracer design of our measurements. When the transfer velocities of gases are normalized against the transfer velocity of  $O_2$  (all  $k$ 's corrected for diffusivity), the tight functional relationship between the fluxes of the gases becomes apparent (Figure 2). This relationship indicates that much of the variability of flux at a given wind speed is due to variability in the hydrodynamic forcing of flux. Deviations from the linear relationship of unity slope signify other processes are influencing the transfer of a gas. Careful examination indicates that DMS transfer rates lie slightly below the line at higher wind speed, meaning that DMS behaves somewhat differently than the permanent gases under the experimental temperatures and wind speeds.



**Figure 2** Laboratory wind-wave tank measurements of  $SF_6$ , Ne,  $CH_4$ , DMS, and He transfer velocities ( $Sc=600$ ) versus the transfer velocity of  $O_2$  ( $Sc=600$ ). Data represented as open symbols and solid symbols were measured in fresh water and seawater, respectively. Standard errors are plotted for each data point. The solid line represents ideal "water-side controlled" kinetics. Dashed lines represent predicted  $k_{600}$  for DMS at temperatures 0, 10 and 20°C using our formulation of  $\gamma_a$ .

We evaluated the importance of the two boundary layers by considering the steady state condition in which the mass balance for gases at the interface is given by:

$$m_a'' = m_w'' \quad (1)$$

when the flux through the boundary layers of the air phase and water phase are equal and respectively:

$$m_a'' = k_a(c_a - C_{s,w}/\beta) \quad (2)$$

$$m_w'' = k_w(C_{s,w} - C_w) \quad (3)$$

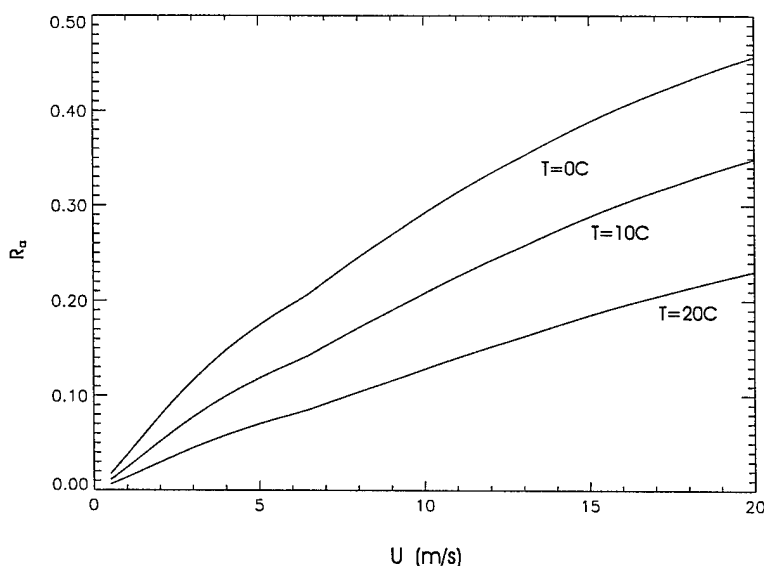
where  $c_a$  and  $C_w$  are bulk concentrations in the air and water,  $C_{s,w}$  is gas concentration at the interface between the water surface and air expressed in terms of aqueous concentration, and  $\beta$  is the Bunsen coefficient (expressed as the ratio  $C_w/c_a$  at equilibrium). The transfer velocities,  $k_a$  and  $k_w$ , are expressions of the hydrodynamic regime in the air and water boundary layers. We combine eqns. (1), (2), and (3) to determine the relative importance of the air-surface concentration difference to the water-surface concentration difference in controlling flux. This ratio becomes:

$$\frac{\beta c_a - C_{s,w}}{C_{s,w} - C_w} = \frac{\beta k_w}{k_a} \quad (4)$$

Using the fact that the sum of the air fraction and water fraction is unity allows equation 4 to be arranged, yielding the ratio of the air concentration difference to the total concentration difference,  $\gamma_a$ , given as:

$$\gamma_a = \frac{\beta c_a - C_{s,w}}{\beta c_a - C_w} = \frac{1}{1 + k_a/\beta k_w} \quad (5)$$

$\gamma_a$  is the air-side gradient fraction, defined as the gas concentration gradient across the air-side sublayer layer as a fraction of the entire gradient from the bulk water to the bulk air. When  $k_a$  is small, or when solubility is high,  $\gamma_a$  approaches unity. As such, therefore,  $\gamma_a$  is a measure of the error in assuming the flux is water-side controlled. To date,  $k_a$  and  $k_w$  have not been



**Figure 3** The air-side gradient fraction,  $\gamma_a$ , for DMS as a function of wind speed at temperatures 0, 10, and 20°C in seawater are shown.  $\gamma_a$  is determined from  $\beta$ ,  $k_w$ , and  $k_a$  as shown in equation 5. Values of  $\beta$  come from Dacey *et al*, 1984. Values of  $k_w$  and  $k_a$  are determined from tank experiments. The value of  $k_w$  is determined from sparingly soluble gases and the value of  $k_a$  is determined from water vapor transport (e.g., Kondo 1975). The increase in  $\gamma_a$  with wind speed arises because  $k_w$  increases faster with increasing wind speed than  $k_a$ . Decreasing temperature raises gas solubility, leading to an increase in  $\gamma_a$ .

quantified simultaneously in oceanic conditions. *In situ* values of  $k_a$  (e.g., Kondo, 1975) and  $k_w$  can be approximated from available models.

Due to the moderate solubility of DMS (Dacey et al., 1984),  $\gamma_a$  becomes significant at lower water temperatures. Also, increasing wind speed has a greater influence on the aqueous sublayer than on the air-side sublayer, with the result that  $k_a$  becomes increasingly important at higher wind speeds. These findings are summarized in Figure 3, which shows the influence of temperature and wind speed on  $\gamma_a$ . We conclude that air-side control may be a significant factor in higher latitudes where DMS is commonly found at high concentrations in surface water (Berresheim, 1987), and where both low temperatures and high winds are typical. As  $\gamma_a$  approaches 0.4, conventional flux models based on wind speed parameterizations may overestimate DMS flux for these locales by 60%.

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Publications from this project:

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Presentations:

Dacey, J. W. H., N. M. Frew, E. J. Bock, W. R. McGillis, Water-Air Transfer of  
Dimethylsulfide," ASLO Aquatic Sciences Meeting, Sante Fe, February, 1996.

Dacey - Dimethylsulfide: A geophysiology of the surface ocean. University of Connecticut  
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